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## ABSTRACT (Maximum 200 words)

The research performed on this grant began with the study of CdS quantum dots in a sol-gel host as an enhancement to semiconductor-doped glass systems. The CdS dots were synthesized via inverse-micellar chemistry, which is shown to be capable of compositionally-homogeneous semiconductor colloids. The results involving synthesis and optical characterization of solution-derived, quantum-dot-doped materials is discussed, including preliminary results on transition-metal doping of CdS dots. The final year of the grant was focused on the growth of nanostructures on glass substrates by pulsed-laser deposition (PLD). A series of thin films composed of binary through quaternary II-VI semiconductors were deposited on silica substrates. The work includes deposition from stoichiometric PLD targets as well as targets which were alternated to achieve the desired stoichiometry. The films were characterized by absorption spectroscopy.

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**Final Report:**

**Development of Novel Optical Materials  
via Quantum Dot-Doped Sol-Gel Hosts**

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**Oklahoma State University**

**92-J-0428**  
**AFOSR Grant: F 49620-92-5-1096**

## I Publications and Presentations

A paper entitled: "Optical Characterization of Binary, Ternary and Quaternary II-VI Semiconductor Thin Films Prepared by Pulsed Excimer Laser Deposition" is in press with the SPIE. A copy of this paper is attached.

An oral paper by the same title was given as an invited talk at the LASE '97 conference (San Jose, Feb '97).

## II Research Summary and Introductory Comments

During the project performance period, the AFOSR contract monitor responsibilities were shifted from Lt.Col. G. Pomrenke to Maj. Michael Prarie. The essential theme of the work performed during the final year of the project remained unchanged, but the focus shifted from quantum dots prepared in sol-gel media to complex semiconductor layer compositions prepared by pulsed laser deposition (PLD). PLD methods, which utilize a focused pulsed laser source to photoionize a target having a desired composition, capitalize on highly kinetically-controlled growth characteristics to develop novel compositional and/or structural characteristics. Semiconductor compositions which are difficult or impossible to grow by conventional deposition methods (i.e., ternary or quaternary II-VI semiconductor compositions) are readily deposited by PLD methods.

The focus of the final year of the project reported herein is to produce and characterize the novel materials obtained by placing thin films of II-VI semiconductors, including binary, ternary, and quaternary compositions, upon silica substrates by pulsed laser deposition. This technique allows a high degree of control over film composition. By variation of such processing parameters as laser fluence and pulse count, atmosphere, and target composition a wide range of films can be generated with novel properties.

Pulsed lasers are becoming a popular tool for the deposition of coatings and active layers, as reflected by the rapidly growing body of research in both the fundamentals of pulsed-laser ablation and deposition (PLD) and their applications in the production of thin films.<sup>1</sup>

While there are a number of methods available for the production of thin films, PLD offers significant advantages in several areas of materials research. For example, it is a very promising method for producing complex multicomponent semiconductor films and films requiring the creation of epitaxial-superlattice or quantum-well heterostructures. Advantages include (1) the ability to transfer material from a polycrystalline target to a substrate while retaining the stoichiometry of the target; (2) the enhancement of the formation of crystals or epitaxial layers due to the energetic nature of PLD material transfer processes and consequently enhanced surface diffusion; (3) the ability to control the reaction atmosphere and thereby influence the products; and (4) the availability of a large degree of precision in controlling film thickness by controlling the operating parameters of the laser.<sup>2</sup>

When applied to semiconductors, PLD can produce materials with a wide range of energy band gaps and lattice constants for photovoltaic and optoelectronic device structures.<sup>2-3</sup> The flexibility of PLD is further enhanced when combined with a multiple-target carousel, which allows the preparation of layered structures (e.g. quantum-well and epitaxial-superlattice structures) by switching targets at controlled intervals. Careful tailoring of the layers can result in the matching of a desired lattice constant or band-edge offset in adjacent layers and can thereby increase the range of band gaps and lattice constants available. Such layered structures are readily achieved with PLD; they are very difficult to grow by such methods as chemical vapor deposition because of the necessity of maintaining control over a large number of independent input fluxes.<sup>2,4-5</sup>

The II-VI family of semiconductors, most members of which have moderate to wide energy band gaps, finds use in optically active devices ranging from diodes and lasers for displays and communications to photovoltaic energy conversion.<sup>2</sup> A number of them have been deposited on various substrates, usually other semiconductors, by PLD in recent years.<sup>4-8</sup>

In the present study, a series of thin films composed of binary, tertiary, and quaternary II-VI semiconductors was coated onto silica substrates by the PLD technique. Both films produced from semiconductor targets already containing the desired final stoichiometry and films made by depositing alternating layers from targets of different semiconductor compositions were included. This work focuses upon the preparation of compositionally complex semiconductor layers, which have been preliminarily characterized using absorption spectroscopy.

- I. Preliminary photoluminescence emission and excitation spectroscopy of the semiconductor-film-on-silica composites were found to be inconclusive and difficult to interpret in any qualitative manner. For this reason, absorption spectroscopy proved to be a better optical characterization method for these composites. Furthermore, the use of absorption spectroscopy has not been widely exploited in studies of semiconductor films because the vast majority of such studies have focused on coating substrates of silicon or other semiconductor substrates (e.g. for photovoltaic applications) which are not compatible with ultraviolet/visible/near-infrared absorption spectroscopy.<sup>2-3,6-7</sup> Its utility in characterizing II-VI films on transparent substrates has, however, been previously reported for a CdS/quartz system<sup>9</sup> and for  $Zn_xCd_{1-x}Se$  ( $0 \leq x \leq 1$ ) films on glass.<sup>10</sup> In both cases absorption spectroscopy provided useful information about the materials' optical transitions and band structure.

### **III. Experimental Methods**

#### **A. Specimen Preparation**

The semiconductor-on-silica films characterized herein were produced by ablating a semiconductor target with pulsed ultraviolet laser radiation and then condensing material from the resulting ablation plume onto a heated silica substrate. Both target and substrate were confined within a vacuum deposition chamber. Target and substrate carousels and the vacuum chamber were designed and constructed at Oklahoma State University. These were used

according to the schematic representation given in Figure 1. Prior to irradiation, the assembled chamber components were evacuated to less than  $3 \times 10^{-6}$  torr, then purged with dry nitrogen to desired operating pressures of less than  $3 \times 10^{-4}$  torr.

Semiconductor target compositions of the included zinc sulfide and zinc selenide obtained from II-VI, Inc., and zinc cadmium selenide ( $Zn_{0.5}Cd_{0.5}Se$ ) and cadmium selenide obtained from Electronic Space Products International (ESPI). All targets were used as received. Both targets and substrates were rotated during PLD at a rate of about 40 rpm. Compositions of deposited films included those of the procured targets, as well as a quaternary zinc cadmium sulfide selenide ( $Zn_{1.5}Cd_{0.5}SSe$ ) prepared using a combination of target sources. Processing parameters for the film specimens discussed herein are listed in Table 1.

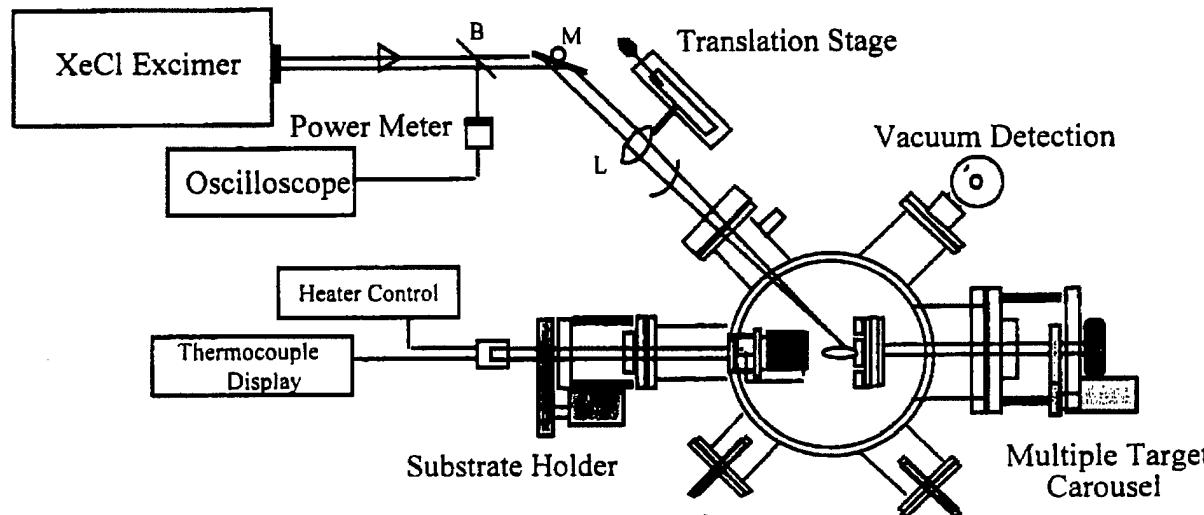


FIGURE 1: Vacuum chamber and laser setup (B = beam splitter, M = mirror).

TABLE I

Composition	ID	$T_s$ (°C)	$\Phi$ (J/cm <sup>2</sup> )	$d_{ts}$ (mm)	$n_p$	$P$ (torr N <sub>2</sub> )
ZnS	#1	220	0.50	40	15,000	$1.3 \times 10^{-4}$
ZnS	#2	300	0.75	40	15,000	$1.3 \times 10^{-4}$
ZnSe	#1	310	1.00	40	8,000	$1.4 \times 10^{-4}$
ZnSe	#2	300	1.00	40	12,000	$1.4 \times 10^{-4}$
CdSe	#1	315	1.00	40	12,000	$2.0 \times 10^{-4}$
CdSe	#2	310	0.75	40	14,400	$2.0 \times 10^{-4}$
CdSe	#3	310	1.00	40	9,400	$2.0 \times 10^{-4}$
$Zn_{0.5}Cd_{0.5}Se$	#1	320	0.50	35	12,000	$2.6 \times 10^{-4}$
$Zn_{0.5}Cd_{0.5}Se$	#2	310	0.75	40	12,000	$2.0 \times 10^{-4}$
$Zn_{1.5}Cd_{0.5}SSe$	#1	300	0.75	50-55	$1,200 \times 10$	$1.9 \times 10^{-4}$
$Zn_{1.5}Cd_{0.5}SSe$	#2	300	0.75	30-35	$600 \times 16$	$1.0 \times 10^{-4}$

TABLE 1: Specimen processing parameters, where  $T_s$  is the substrate temperature in °C,  $\Phi$  is the laser fluence in J/cm<sup>2</sup>,  $d_{ts}$  is the target–substrate separation distance in mm,  $n_p$  is the laser pulse count, and  $P$  is the chamber pressure in torr of nitrogen.

The target irradiation source was a Lambda Physik LEXtra 200i xenon chloride excimer laser operating at a wavelength of 308 nm and modified to oscillate with a temporal pulse width of 10 ns. Nominal energy output from this source was about 200 mJ per pulse. Its energy output was measured with a Molelectron J50 joulemeter probe coupled to a Tektronic TDS 640A oscilloscope. The laser pulses were focused onto the target through a fused silica window in the vacuum chamber and a fused silica lens (focal length 30 cm), the position of which could be varied by translator stage. Variable spot sizes and power outputs were used to produce laser fluences between 0.50 and 1.00 J/cm<sup>2</sup>.

#### B. Film Characterization

Continuous-wave room-temperature absorption spectra were measured using a Varian Cary 5E spectrophotometer, software-corrected for instrumental response and calibrated internally to the lines of its D<sub>2</sub> lamp.

### IV. Discussion of Results

#### C. Zinc Sulfide

The two ZnS films were both a transparent pale yellow with thin-film interference fringes visible both upon visual inspection and in the absorption spectra presented in Figure 2. Similar interference fringes were observed by Kwok *et al.* in their CdS films on quartz; they are attributable to the proper combination of thickness and difference in refractive index between film and substrate to cause optical interference.<sup>9</sup> The sharp band edges near 3.5 eV (360 nm) are in good agreement with the bulk band gap energy ( $E_g$ ) value of 3.54 eV (356 nm).<sup>11</sup>

There are two observable differences in the spectra of films ZnS #1 and #2. First, the interference fringes are much less pronounced in #2 than in #1. Second, the slope of the band edge of #2 is higher than that of #1 and its spectrum reaches the plateau of maximum resolvable absorption (the resolution limit of this particular spectrophotometer) about 0.1 eV before that of #1. Both of these factors are consistent with film #2 having a greater optical path length and therefore thickness than #1. Combined with the difference in fringe effects, this band edge observation indicates that film #2 is thicker than #1, almost too thick to generate interference fringes.

The differences in processing conditions between #1 and #2 are increases in substrate temperature ( $T_s$ ) and laser fluence ( $\Phi$ ) from #1 to #2. As will also be discussed in sections 3.4 and 3.5, increases in  $\Phi$  were observed to be associated with increases in film thickness. The

initial deposition trials in this study demonstrated that higher substrate temperatures led to better adhesion of the film to the substrate, hence the ability to prepare to thicker films. The processing trends therefore correlate well to the spectroscopic observations.

#### D. Zinc Selenide

Like the yellow ZnS films (§3.1), both pale-orange ZnSe films were transparent with visible interference fringes. The absorption spectra presented in Figure 3 show the onset of band edges near 2.5 eV (500 nm) for both ZnSe films, which reasonably approximates the bulk  $E_g$  value of 2.58 eV (488 nm).<sup>11</sup>

As was the case for the ZnS films, there are two observable differences in the spectra of ZnSe films #1 and #2. First, the interference fringes in this case are much less pronounced in #1 than in #2 (the reverse of the ZnS case). Second, the slope of the band edge of #2 is higher than that of #1 and its spectrum reaches an absorption plateau (but still within the instrument's resolution limit), whereas the spectrum of #1 does not reach a plateau solely attributable to the ZnSe film. Instead, it becomes convoluted with the onset of a strong absorption band centered near 5.0 eV (250 nm) arising from the silica substrate.<sup>12</sup> As was the case with the ZnS films, these factors are consistent with the ZnSe film #2 having a greater thickness than #1, which is in fact almost too thin to generate interference fringes.

The only significant difference in processing conditions between ZnSe #1 and #2 is the pulse count ( $n_p$ ), but that difference is substantial because the count of #1 is only 2/3 that of #2, and film thickness is expected to be a nearly linear function of  $n_p$ .

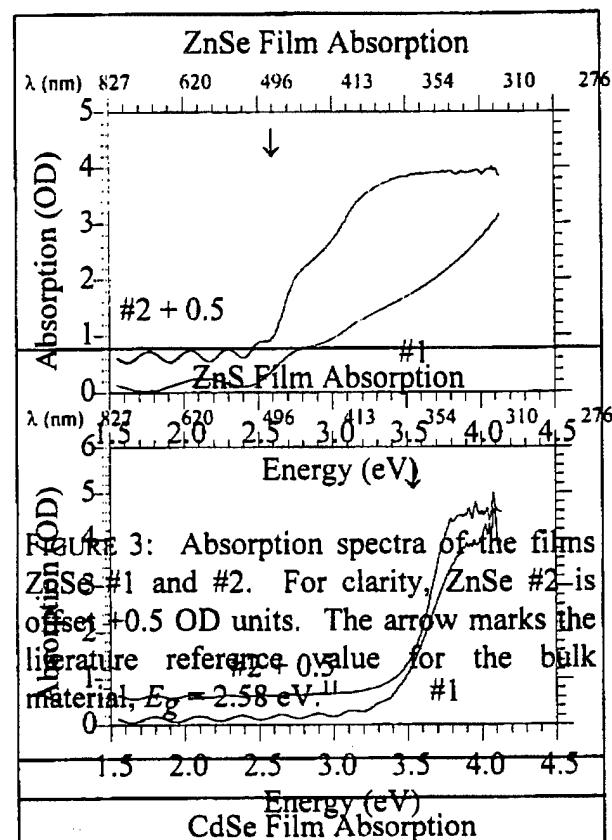


FIGURE 3: Absorption spectra of the films ZnSe #1 and #2. For clarity, ZnSe #2 is offset +0.5 OD units. The arrow marks the literature reference value for the bulk material,  $E_g = 2.58$  eV.<sup>11</sup>

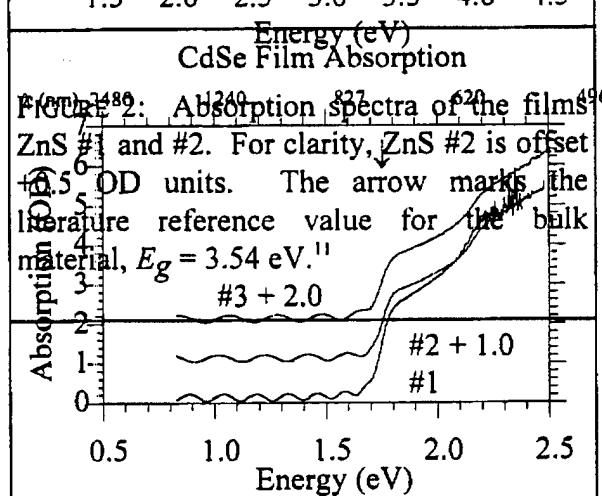


FIGURE 4: Absorption spectra of the films CdSe #1, #2, and #3. For clarity, CdSe #2 and #3 are offset +1.0 and +2.0 OD units, respectively. The arrow marks the literature reference value for the bulk material,  $E_g = 1.74$  eV (724 nm).<sup>11</sup>

The substantial difference in the absorption spectra of the two ZnSe films resulting from a change in a single process variable shows that the optical properties of the films depends quite strongly upon the pulse count and its correlation to film thickness.

### E. Cadmium Selenide

In contrast to the preceding two materials, the CdSe films had a dark gray appearance with a metallic luster like that of silicon. Their absorption band edges and interference fringes are not apparent to the observer, but are readily discernible from the absorption spectra presented in Figure 4. The band edges of all three CdSe films are sharply defined and lie near 1.7 eV (730 nm), in agreement with the bulk  $E_g$  value of 1.74 eV (724 nm).<sup>11</sup>

For the three CdSe films, variations in band-edge behavior lead most readily to the interpretation of differences among their spectra. The spectra of films CdSe #2 and #3 are almost identical, leading to the conclusion that the films themselves are essentially identical. The slope of the band edge of CdSe #1 is higher than those of #2 and #3 and its spectrum reaches the instrument's resolution limit at 2.2 eV, whereas those of #2 and #3 reach the resolution limit at about 2.5 eV. Film CdSe #1 is therefore thicker than #2 and #3, which have essentially the same thickness.

The processing parameters in which there are variations among the three CdSe films are the laser fluence ( $\Phi$ ) and the pulse count ( $n_p$ ). Those values are 1.00 J/cm<sup>2</sup> and 12,000 pulses for CdSe #1, 0.75 and 14,400 for #2, and 1.00 and 9,400 for #3 (see Table 1). Comparison of the two CdSe films with matching fluences, #1 and #3, reinforces the direct relationship between  $n_p$  and film thickness observed in the ZnSe films (§3.2). Using CdSe #1 as a reference, changes in its  $\Phi$  and  $n_p$  values by factors of 0.75 and 1.2, respectively, in the deposition of #2 produced the same result that a change in  $n_p$  alone by a factor of 0.78 did in the deposition of #3. Therefore, over this range of values fluence is also directly related to film thickness, and in at least this case has a stronger influence on film thickness and the resultant optical properties than does the pulse count.

### F. Zinc Cadmium Selenide

The  $Zn_{0.5}Cd_{0.5}Se$  films #1 and #2 had a dark red appearance. Their absorption band edges and interference fringes are apparent to the observer and on the absorption spectra presented in Figure 5. The band edges of  $Zn_{0.5}Cd_{0.5}Se$  #1 and #2 originate near 1.9 eV (650 nm), which

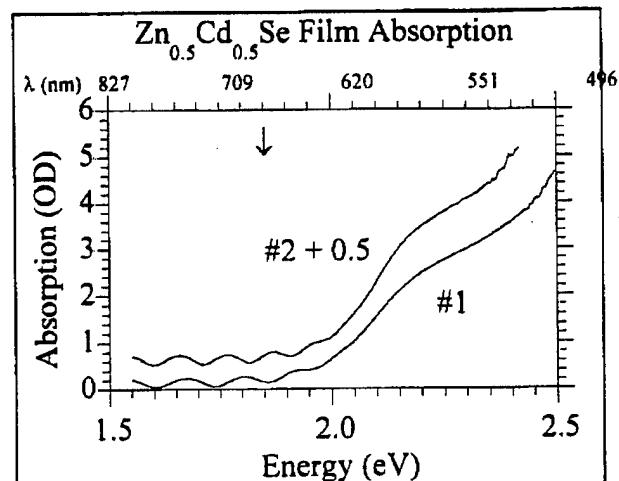


FIGURE 5: Absorption spectra of the films  $Zn_{0.5}Cd_{0.5}Se$  #1 and #2. For clarity, the spectra of #2 is offset +0.5 OD units. The high-energy ends of both spectra terminate where the instrument resolution limit was exceeded. The arrow marks the reference value for the bulk material,  $E_g = 1.85$  eV (670 nm), as calculated via the method of Gupta *et al.*<sup>10</sup>

corresponds well to the  $E_g$  value of 1.85 eV (672 nm) calculated by the authors after Equation (6) of Gupta *et al.*:<sup>10</sup>

$$(1) \quad E_g(x) = E_2 + (E_1 - E_2 - b)x + bx^2$$

where  $E_1$  and  $E_2$  are the band gaps of ZnSe ( $x = 1$ ) and CdSe ( $x = 0$ ), respectively,  $b = 1.26$  is the "bowing parameter," and  $x = 0.5$ .

As for the CdSe films (§3.3), variations in band-edge behavior lead most readily to the interpretation of differences among the spectra of  $Zn_{0.5}Cd_{0.5}Se$  films #1 and #2. While their spectra are similar, the slope of the band edge of  $Zn_{0.5}Cd_{0.5}Se$  #2 is somewhat higher than that of #1 and its spectrum reaches the instrument resolution limit about 0.1 eV before that of #1. Film  $Zn_{0.5}Cd_{0.5}Se$  #2 is therefore somewhat thicker than #1.

The processing parameters which vary between films  $Zn_{0.5}Cd_{0.5}Se$  #1 and #2 are the fluence and the target-substrate separation ( $d_{ts}$ ), 0.50 J/cm<sup>2</sup> and 35 mm for #1 and 0.75 and 40 for #2 (see Table 1). As seen in CdSe, increasing  $\Phi$  increases the film thickness, but in this case the difference in thickness arising from the change in  $\Phi$  values is reduced because of the decrease in  $d_{ts}$ , because  $d_{ts}$  is expected to have an inverse relationship with film thickness.

#### G. Zinc Cadmium Sulfide Selenide

In contrast to the preceding materials which were formed by the ablation of single targets, the films with the nominal composition of  $Zn_{1.5}Cd_{0.5}SSe$  were formed from the alternation of the ZnS and  $Zn_{0.5}Cd_{0.5}Se$  targets. To the best of the authors' knowledge this particular film-substrate composition has not been previously described in the literature. To the observer the films, especially #2, have a "bull's-eye" appearance, with alternating concentric bands of color ranging from dark red to yellow, and this effect appears as strong interference fringes between 1.5 and 2.0 eV in Figure 6. The band edges of both films show signs of convolution of more than one absorption band and their slopes are fairly shallow relative to the previously described materials. The onset of the band edge, obtained by tracing a line tangent to the apparent band edge to its intersection with the abscissa, provides an estimated  $E_g$  of 1.8 to 1.9 eV (650 to 690 nm), much closer to the value of CdSe than to ZnS.

The spectra of films  $Zn_{1.5}Cd_{0.5}SSe$  #1 and #2 are similar, but the band edge slope of #2 is noticeably higher than that of #1, and the spectrum of #2 reaches the instrument's resolution

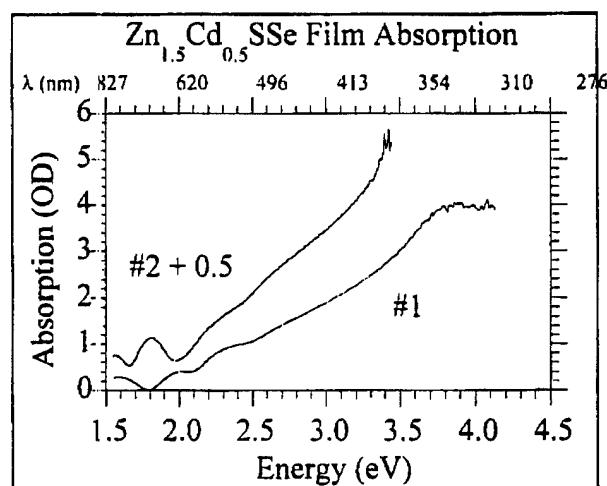


FIGURE 6: Absorption spectra of the films  $Zn_{1.5}Cd_{0.5}SSe$  #1 and #2. For clarity, #2 is offset +0.5 OD units. The high-energy end of spectrum #1 terminates where instrument resolution limit was exceeded.

limit about 0.3 eV before that of #1 reaches its plateau. Film  $Zn_{1.5}Cd_{0.5}SSe$  #1 is therefore thicker than #2.

The main differences in their processing are that  $Zn_{1.5}Cd_{0.5}SSe$  #1 was constructed from 10 iterations of 1,200 pulses each (12,000 total pulses in 5 cycles) while #2 was constructed from 16 iterations of 600 pulses each (9,600 total pulses in 8 cycles), and in #2 the substrate was about 40% closer to the target than in #1. As has been discussed in the sections above, increases in pulse count and decreases in target-substrate separation are associated with increased film thickness; in this case, in #2 the effect of decreased  $d_{ts}$  apparently compensates that of decreased  $n_p$  relative to #1. Differences in composition between the two films as a result of layer spacing are not spectroscopically evident.

## V. Conclusions, Absorption Spectroscopy Studies

The spectroscopic evidence is clear that using PLD to construct II-VI semiconductor films on silica produces new materials with properties significantly different from the starting materials, and one such quaternary composition is described herein. By controlling the laser processing parameters, a variety of films can be made from a single target, in a range of thicknesses from much less than the wavelengths of visible light to thicknesses which produce measurable interference. By introducing a multiple-target carousel into the system, completely new materials may be constructed with new optical properties, as evidenced by the differences between the spectra of the layered  $Zn_{1.5}Cd_{0.5}SSe$  films and their precursors. The potential applications of this technique in photovoltaic and optoelectronic device structures have only begun to be explored.

## VI. Other Studies

A large number of additional II-VI thin-film specimens were prepared in the custom-built vacuum chamber by ablating the surface of a solid II-VI target with the focused UV (308 nm) laser radiation of a Lambda Physik LEXtra xenon chloride excimer laser (10-ns pulse width, 20-Hz repetition rate). Both the target and the substrate were rotated to evenly distribute the ablation damage and plume products. In all of the trials except the first two the substrate was heated to at least 300°C to enhance film adhesion. The target carousel was constructed to hold up to four separate targets for the deposition of multiple layers of differing composition.

Specimen creation to date has focused upon observing the effects of variation in such parameters as target composition, number and thickness of alternating film layers, substrate temperature ( $T_S$ ), laser fluence ( $F$ ), substrate-target separation ( $d_{ST}$ ), and the chamber pressure ( $P$ ) and atmosphere. These parameters are summarized in Table 1, which displays the target and film empirical formulas and the current condition of the specimen, and Table 2, which displays the laser parameters (fluence and the pulse count) and chamber parameters ( $T_S$ ,  $d_{ST}$ , and  $P$ ).

Early results clearly showed that heating the silica substrate was desirable for film adhesion. Most of the samples produced at higher  $T_S$  have proved to be stable after several weeks of storage in a glove box with a primarily N<sub>2</sub> atmosphere. Attempts to overcoat the II-VI film (in which S<sup>2-</sup> and Se<sup>2-</sup> are subject to attack by O<sub>2</sub> at moderate rates) with a protective layer of silica or borosilicate glass have not yet proved effective, tending to remove the film. While several such specimens have been excluded, LR10 has been included specifically to show the results of such an overcoat failure.

**Table 1: Compositions and Current Status**

Sample ID	Target Formula	Specimen Formula	Specimen Current Status
LR1	ZnS	ZnS	Completely webbed, second spectrum not run
LR2	ZnS	ZnS	Center flaked off, spectra run at edge
LR3	ZnS	ZnS	Good (broken for LT)
LR4	ZnS	ZnS	Slightly webbed (broken for LT)
LR5	$Zn_{0.5}Cd_{0.5}Se$	$Zn_{0.5}Cd_{0.5}Se$	Good
LR6	$Zn_{0.5}Cd_{0.5}Se$	$Zn_{0.5}Cd_{0.5}Se$	Good
LR7	$Zn_{0.5}Cd_{0.5}Se + ZnS$	$Zn_{1.5}Cd_{0.5}SSe$	Slightly webbed
LR8	$Zn_{0.5}Cd_{0.5}Se + ZnS$	$Zn_{1.5}Cd_{0.5}SSe$	Good
LR9	ZnSe + CdSe	$Zn_{0.5}Cd_{0.5}Se$	Good
LR10	$Zn_{0.5}Cd_{0.5}Se$	$Zn_{0.5}Cd_{0.5}Se$	Center flaked off by attempt to overcoat with glass
LR11	ZnSe	ZnSe	Good
LR12	ZnSe	ZnSe	Good
LR13	CdSe	CdSe	Good
LR14	CdSe	CdSe	Good
LR15	CdSe	CdSe	Good except for a few scratches

**Table 2: Deposition Parameters**

ID	$F$ (J/cm <sup>2</sup> )	Pulses	$T_S$ (°C)	$dST$ (mm)	$P$ (μtorr)	
LR1	2.00	18,000	RT	40	52	Air
LR2	2.00	18,000	RT	40	52	Air
LR3	0.50	15,000	220	40	134	N <sub>2</sub>
LR4	0.75	15,000	300	40	130	Air
LR5	0.50	12,000	318–324	35	260	N <sub>2</sub>
LR6	0.75	12,000	300–315	40	200	N <sub>2</sub>
LR7	0.75	1,200 × 10	300	50–55	190	N <sub>2</sub>
LR8	0.75	600 × 16	300	30–35	100	N <sub>2</sub>
LR9	0.75	1,000 × 10	300	35	100	Air
LR10	0.75	12,000	318–324	35	260	N <sub>2</sub>
LR11	1.00	8,000	310	40	140	Air
LR12	1.00	12,000	300	40	140	N <sub>2</sub>
LR13	1.00	12,000	310–320	40	200	N <sub>2</sub>
LR14	0.75	14,400	310	40	200	N <sub>2</sub>
LR15	1.00	9,400	310	40	200	N <sub>2</sub>

## II. Characterization by UV/VIS/NIR Absorption Spectra

The II-VI film specimens have proved to be readily characterizable by UV/VIS/NIR absorption spectroscopy as illustrated in the following seven figures. Figures 1 and 2 display the spectra of the zinc sulfide target and four films shortly after deposition (Fig. 1) and several weeks later (Fig. 2). The relatively insignificant variation of the spectra with time shows encouraging stability upon storage in a nominally oxygen-free atmosphere. All of the films in this study show noticeable interference fringes and their band edges are blue-shifted relative to the bulk material, indicating the onset of quantum confinement.

Figure 3 displays the spectra of the zinc selenide target (remarkably transparent as it is over 1 cm wide) and two films which differ chiefly in pulse count (8k and 12k, respectively) and therefore thickness.

Figure 4 displays the spectra of four different zinc cadmium selenide ( $Zn_{0.5}Cd_{0.5}Se$ ) films. The spectral pairs A-B and C-D demonstrate a high degree of stability of films LR5 and LR6, whose small difference is due to variations in fluence and  $d_{ST}$ . LR9 is significantly different as it was constructed from two different layers (ZnSe and CdSe), where LR5 and LR6 were constructed from a single ternary target. LR10 shows a relatively high degree of transparency due to most of its II-VI film being removed by the overcoating attempt.

Figure 5 displays the spectra of two quaternary  $Zn_{1.5}Cd_{0.5}SSe$  films constructed from alternating layers from the ZnS and  $Zn_{0.5}Cd_{0.5}Se$  targets with differences in  $d_{ST}$  and pulse count. The band edge is very gradual, presumably a convolution of the layer influences, preventing the estimation of a reliable band gap. Both films are once again stable with respect to storage time. Figure 6 shows the effects of thin-film interference in measuring the absorption spectra of LR8, which has a marked "target" structure of concentric interference fringes.

Figure 7 displays the spectra of three cadmium selenide films which differ primarily in fluence and pulse count. The spectral axis is shifted to longer wavelengths than those in Figures 1-6 due to the lower bandgap energy of CdSe relative to the zinc compounds.

## III. Future Work

A. *Fluorescence Spectroscopy.* Room- and liquid-nitrogen-temperature fluorescence spectroscopy studies of the II-VI films produced to date have already been initiated. Early results indicate that the fluorescence of these specimens is quite weak, causing signal resolution difficulties, but they appear to contain some features unique to the composite structure, *i.e.* not present in either the bulk II-VI semiconductor or the silica substrate. In particular, the application of the film appears to create luminescence bands characteristic of silica defects which are not present in the uncoated silica substrate.

B. *Capping.* While the attempts made so far to overcoat II-VI films with dielectrics have not so far proved successful, further refinements of the technique should lead to success in this area in the near future. Such success will lead to possibilities of long-term stability in air as well as enhanced possibilities of obtaining quantum-confined materials.

C. *Other Compositions.* The complete range of compositions available to us even while restricted to the commercially-available binary and ternary compositions has not yet been explored. Targets of other II-VI compositions, especially those containing mercury or tellurium, or more than three components, are either not available commercially or the cost of target pressing is prohibitive, so studies of these must await the purchase of a hot isostatic press.

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